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OFFICE OF NAVAL RESEARCH

END-OF-THE-YEAR REPORT

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

GRANT or CONTRACT: N00014-91-J-1934

R&T Code 4132060

Alumoxanes: Rationalization of Black Box Materials

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Date Submitted:  
May 18, 1993

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## PART II

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- c) Cognizant ONR Scientific Officer: Dr. K. Wynne
- d) Description of project:

Alumoxanes are defined as oligomeric or polymeric materials consisting of an Al-O backbone with pendant organic substituents. Despite having a diverse range of applications, including components in catalytic systems and preceramic precursors little is understood of their structure or chemical properties and characteristics. The purpose of this study is to; (a) confirm our previous proposal as to the three dimensional structure of the Al-O backbone (or core) of alumoxanes, (b) develop new and improved synthesis of alumoxanes, particular emphasis being placed on the ability to control physical properties, and (c) determine the structural motifs present in alkyl alumoxane catalysts such as methylalumoxane, MAO.

## e) Significant Results

Methylalumoxane,  $(\text{MeAlO})_n$  or MAO, has been proposed to exist as cyclic or linear structures. We have been the first to show that, by the synthetic analogue approach, alkyl alumoxanes are three dimensional clusters, thus confirming our previous proposal that all alumoxanes are cluster species. X-ray crystallographic evidence for the hexameric, octameric and nonameric forms of *tert*-butyl alumoxane,  $[(^t\text{Bu})\text{AlO}]_n$ , have been obtained. In addition, we have isolated the first example of an alkyl alumoxane containing a highly Lewis acidic three coordinate aluminum center.

Initial results indicate that our isolable *tert*-butyl alumoxanes are active cocatalysts in a number of polymerization systems. Thus, they represent very accurate models for the mixture of species present in MAO.

Our most important result has been to demonstrate that the *tert*-butyl alumoxanes show unique activity as co-catalysts with palladium complexes for the synthesis of polyketones,  $[\text{CH}_2\text{CH}(\text{R})\text{C}(\text{O})]_n$ . The activity observed is comparable to commercial systems but without the instability issues (see below).

Commercial samples of polyketones suffer from severe thermal decomposition during melt processing. The Patent literature describes the use of hydrolyzed  $\text{Al}(\text{O}^i\text{Pr})_3$  as a good stabilizing agent. Since we have demonstrated that hydrolyzed alkoxides are alumoxanes with a core structure of boehmite, we reasoned that boehmite itself would be more effective. This is indeed the case. However, based on our previous work with the reaction of boehmite with carboxylic acids we have determined that the most effective stabilization agents are alumoxanes made from boehmite and 1% carboxylic acid.

A detailed study has been undertaken on the equilibria present for  $\text{Me}_2\text{Al}(\text{OR})$  in solution. Importantly it has been shown that both dimeric and trimeric species are present.

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f) Summary for Next Year's Work

In the next year we propose to capitalize on our new synthetic routes to alkyl alumoxanes.

With our isolation of well defined alkylalumoxanes we propose to determine the catalytic activity of these materials both as polymerization catalysts themselves and also as Kaminsky co-catalysts with  $\text{Cp}_2\text{ZrMe}_2$ . We propose to synthesis single alumoxane species and determine their relative effectiveness as catalysts. In this way we will be able to determine the effect of the alumoxane structure on the activity of catalysis as well as the structure and molecular weight of the polymer.

We intend to further our work with the catalytic synthesis of polyketones. We will optimize the polymerization conditions as well as investigate the mechanism of initiation.

With all the catalytic systems we will try and isolate transition metal compound-alkylalumoxane complexes.

g) Chris Landry (Graduate)

Allen Apblett (Post-Doctoral)

Mark Mason (Post-Doctoral)

Linda K. Cheatham (Post-Doctoral)

Jason Rogers (undergraduate)

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- a. Number of papers submitted to refereed journals, but not published: 1
- b. \* Number of papers published in refereed journals (for each, provide a complete citation): 3
- c. Number of books or chapters submitted, but not yet published: 0
- d. \* Number of books or chapters published (for each, provide a complete citation): 0
- e. \* Number of printed technical reports/non-refereed papers (for each, provide a complete citation): 0
- f. Number of patents filed: 0
- g. \* Number of patents granted (for each, provide a complete citation): 0
- h. \* Number of invited presentations (for each, provide a complete citation): 3
- i. \* Number of submitted presentations (for each, provide a complete citation): 6
- j. \* Honors/Awards/Prizes for contract/grant employees (list attached): 1

(This might include Scientific Society Awards/Offices, Selection as Editors,  
Promotions, Faculty Awards/Offices, etc.)

- k. Total number of Full-time equivalent Graduate Students and Post-Doctoral associates supported during this period, under this R&T project number:

Graduate Students: 1

Post-Doctoral Associates: 3

including the number of,

Female Graduate Students: 0

Female Post-Doctoral Associates: 1

the number of

Minority\* Graduate Students: 0

Minority\* Post-Doctoral Associates: 0

and, the number of

Asian Graduate Students: 0

Asian Post-Doctoral Associates: 0

- l. \* Other funding (list agency, grant title, amount received this year, total amount, period of performance and a brief statement regarding the relationship of that research to your ONR grant)

\* Use the letter and an appropriate title as a heading for your list, e.g.:

b. Published Papers in Refereed Journals, or, d. Books and Chapters published

Also submit the citation lists as ASCII files, preferably on a 3" or 5" PC-compatible floppy disks

\* Minorities include Blacks, Aleuts, AmIndians, Hispanics, etc. NB: Asians are not considered an under-represented or minority group in science and engineering.

b) Papers published in refereed journals

1. The Preparation of  $(\text{Al}_2\text{O}_3)_x(\text{SiO}_2)_y$  Thin Films Using  $[\text{Al}(\text{OSiEt}_3)_3]_2$  as a Single-Source Precursor  
C.C. Landry, L.K. Cheatham, A.N. MacInnes, and A.R. Barron, *Adv. Mater. Optics and Electronics*, 1992, **1**, 3-15.
2. Dimethylaluminium Alkoxides: A Physicochemical Study.  
J.H. Rogers, A.W. Apblett, W.M. Cleaver, and A.R. Barron, *J. Chem. Soc., Dalton Trans.*, 1992, 3179.
3. Synthesis and Characterization of Triphenylsiloxy-Substituted  
A.W. Apblett, A.C. Warren, and A.R. Barron, *Can. J. Chem.*, 1992, **70**, 771.
4. Hydrolysis of tri-tert-butyl aluminum: the first structural characterization of alkylalumoxanes,  $[(\text{R}_2\text{Al})_2\text{O}]_n$  and  $[\text{RAlO}]_n$ .  
M.R. Mason, J.M. Smith, S.G. Bott, and A.R. Barron, *J. Am. Chem. Soc.*, 1993, (June issue)

j) Honors/Awards/Prizes

1. Alcoa Foundation Fellowship.

l) Other Funding

Petroleum Research Fund  
Oxidation of Group III Organometallics  
Amount received this year \$18K  
Total amount \$40K  
January 1991 - December 1993

No relationship to ONR

National Science Foundation  
Group 13 Chalcogenides  
Amount received this year; grant started April 1 1993.  
Total amount \$265K  
April 1993 - March 1996

No relationship to ONR

Alumoxanes, what are they ?

**Al-O macromolecules with a general formula  $[\text{Al}(\text{O})_x(\text{OH})_y(\text{X})_z]_n$**

What are their applications ?

X	Known applications	New applications
alkoxide (OR)	alumina precursor, paints	polymer stabilization
siloxide ( $\text{OSiR}_3$ )	aluminosilicate precursor	adhesives
carboxylate ( $\text{O}_2\text{CR}$ )	alumina precursor	polymer stabilizers
chloride	antiperspirant	?
alkyl ( <i>esp.</i> $\text{CH}_3$ )	Ziegler Natta co-catalyst for olefin polymerization	(The first rational model)

What are their structures ?

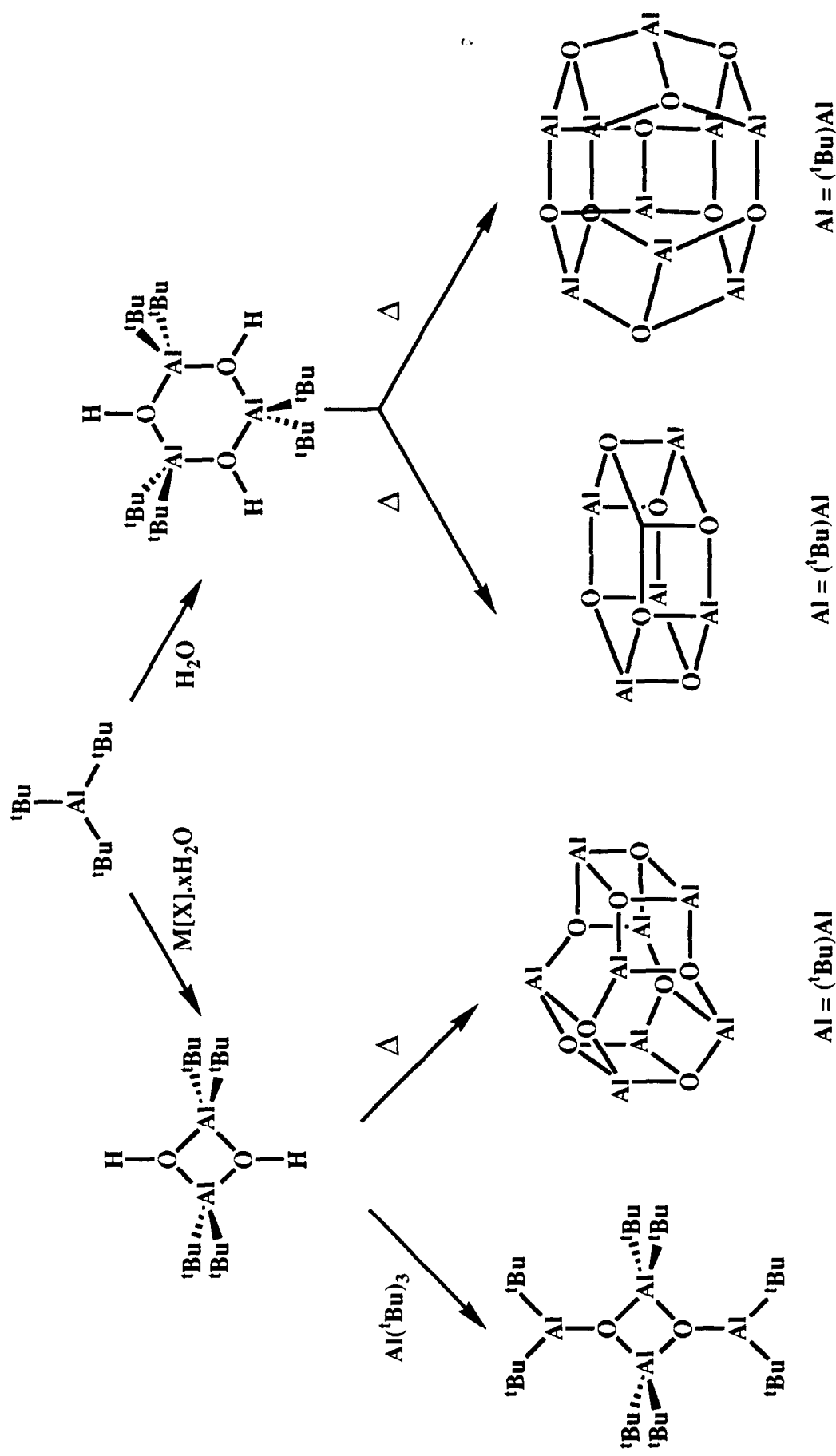
$\text{X} \neq \text{alkyl}$

**Boehmite Core**

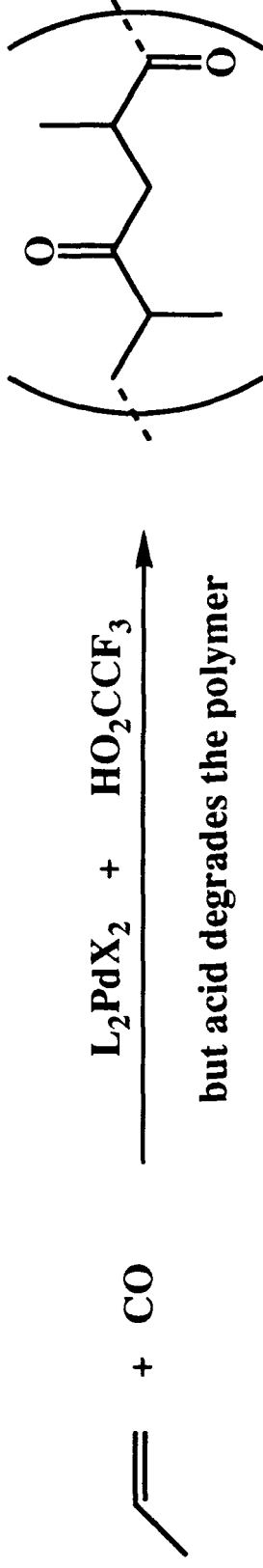
$\text{X} = \text{alkyl}$

**Always assumed linear or cyclic  
but actually clusters**

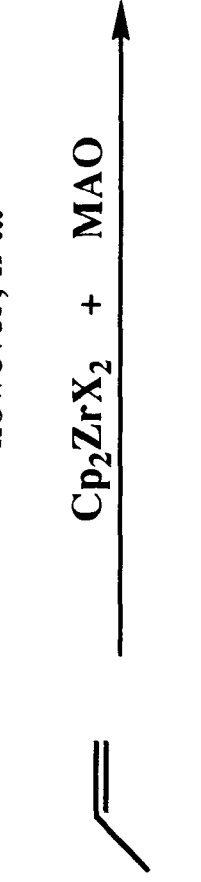
# Synthesis and Structure of Alkylalumoxanes



# New Catalysis with Alkylalumoxanes



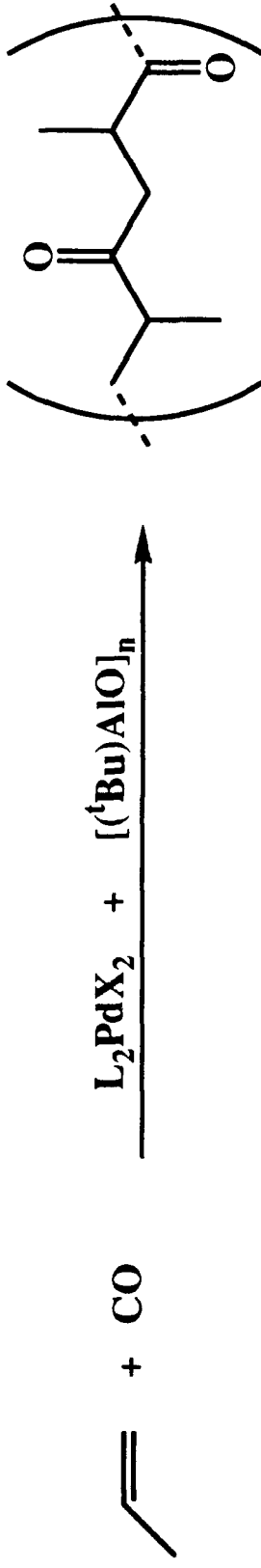
**however, if ...**



**then ...**



So ::





### Explanatory Paragraph

The term alumoxane is used to describe any macromolecule with an aluminum oxygen backbone. A wide range of applications are known (slide 1) and we are developing new uses. Previous workers have suggested a general formula of  $[Al(O)(X)]_n$  where X may be alkyl, alkoxide, siloxide, carboxylate or other organic side chain. We have shown that the stable (non-alkyl) alumoxanes have a general formula  $[Al(O)_x(OH)_y(X)_z]_n$  and have a structure based on that of boehmite  $[Al(O)(OH)]_n$ . In contrast, the alkyl derivatives have until recently eluded characterization despite their application as active polymerization catalysts. We have isolated and crystallographically characterized the first examples of alkyl alumoxanes, and found their structures to be dependent on the synthetic route (slide 2). Polyketone polymers are made commercially by the co-polymerization of CO and olefins using a palladium/tri-fluoroacetic acid catalyst, however, the product is degraded by the acid cocatalyst residues. An alternative non protic acid system should be developed. Using the precedent of zirconocene/MAO olefin catalysis, one may propose a palladium/MAO system, but, this does not give any polymer. However, we have discovered that the new isolable *tert*-butyl alumoxanes must be used (slide 3).

## REPORT DOCUMENTATION PAGE

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Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 5/18/93	3. REPORT TYPE AND DATES COVERED Technical Report
4. TITLE AND SUBTITLE Hydrolysis of Tri- <i>tert</i> -butylaluminum: The First Structural Characterized of Alkylalumoxanes, $[(R_2Al)_2O]_n$ and $(RAIO)_n$ .			5. FUNDING NUMBERS N00014-91-J-1934
6. AUTHOR(S)  Mark R. Mason, Janna M. Smith, Simon G. Bott, and Andrew R. Barron			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Harvard University Department of Chemistry 12 Oxford Street Cambridge, MA 02138			8. PERFORMING ORGANIZATION REPORT NUMBER  3
9. SPONSORING, MONITORING AGENCY NAME(S) AND ADDRESS(ES) Department of the Navy Office of Naval Research 800 North Quincy Street Arlington, VA 22217-5000			10. SPONSORING, MONITORING AGENCY REPORT NUMBER  4132060
11. SUPPLEMENTARY NOTES  Prepared for Publication in J. Am. Chem. Soc., in press			
12a. DISTRIBUTION / AVAILABILITY STATEMENT  Reproduction in whole or in part is permitted for any purpose of the United States government. This document has been approved for public release and sale; its distribution is unlimited.			12b. DISTRIBUTION CODE
13. ABSTRACT (Maximum 200 words) <p><i>Tert</i>-butyl substituted alumoxanes have been prepared and characterized by multinuclear magnetic resonance spectroscopy, mass spectrometry and X-ray crystallography. The low temperature (-78 °C) hydrolysis of <math>Al(^tBu)_3</math> in pentane results in the formation of the trimeric hydroxide <math>[(^tBu)_2Al(\mu-OH)]_3</math> (1) as the major product. Hydrated salt hydrolysis of <math>Al(^tBu)_3</math> in toluene followed by thermolysis of the reaction mixture yields the tetrameric alumoxane <math>[(^tBu)_2Al\{\mu-OAl(^tBu)_2\}]_2</math> (2), and the octameric alumoxane <math>[(^tBu)Al(\mu_3-O)]_8</math> (3). In contrast the thermolysis of 1 yields the hexameric and nonameric alumoxanes, <math>[(^tBu)_4Al(\mu_3-O)]_6</math> (4) and <math>[(^tBu)Al(\mu_3-O)]_9</math> (5). Dissolution of compound 1 in THF or MeCN yields the hydrogen-bound complexes <math>[(^tBu)_2Al(\mu-OH)]_3 \cdot 2(THF)</math> (6) and <math>[(^tBu)_2Al(\mu-OH)]_3 \cdot 2(MeCN)</math> (7) respectively, while no adduct is observed in <math>Et_2O</math> solution. The reaction of 1 with pyridine results in a disproportionation reaction to yield the dimeric compound <math>[(^tBu)_2Al(py)]_2(\mu-O)</math> (8). Compound 8 may be prepared directly from the partial hydrolysis of <math>Al(^tBu)_3</math> in pyridine, in which it exists as the Lewis acid base complex <math>Al(^tBu)_3(py)</math> (9), or from the addition of pyridine to 2. The molecular structures of compounds 1, 2, 4, and 6 - 8 have been determined by X-ray crystallography. The relationship between the <i>tert</i>-butylalumoxanes and the Kaminsky co-catalyst methylalumoxane, MAO, is discussed.</p>			
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4. TITLE AND SUBTITLE Dimethylaluminium Alkoxides: A Physico-chemical Investigation				5. FUNDING NUMBERS N00014-91-J-1934	
6. AUTHOR(S) Jason H. Rogers, Allen W. Apblett, William M. Cleaver, Andrew N. Tyler, and Andrew R. Barron					
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12a. DISTRIBUTION / AVAILABILITY STATEMENT Reproduction in whole or in part is permitted for any purpose of the United States government. This document has been approved for public release and sale; its distribution is unlimited.				12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) Compounds of the type $[\text{Me}_2\text{Al}(\mu\text{-OR})_x]_x$ ( $\text{R} = \text{Me}$ 1, Et 2, $\text{Pr}^n$ 3, $\text{Pr}^i$ 4, $\text{Bu}^n$ 5, $\text{Bu}^i$ 6, $\text{Bu}^s$ 7, $\text{Bu}^t$ 8, $\text{Pent}^n$ 9, $\text{Pent}^i$ 10, $\text{Pent}^{\text{neo}}$ 11, $\text{Hex}^n$ 12, $\text{Oct}^n$ 13, $\text{Dec}^n$ 14, $\text{Dodec}^n$ 15) have been synthesised and studied by $^1\text{H}$ , $^{13}\text{C}$ , $^{17}\text{O}$ and $^{27}\text{Al}$ NMR and IR spectroscopy and mass spectrometry. With the exception of 10, all the compounds with branched chain alkoxide substituents are purely dimeric ( $x = 2$ ), while 10 and the n-alkyl derivatives exist in solution as an equilibrium between dimeric ( $x = 2$ ) and trimeric ( $x = 3$ ) forms. Equilibrium constants, $\Delta H$ and $\Delta S$ for the trimer-dimer equilibria in solution were obtained for 3. These results, and those for the NMR spectroscopic data, are interpreted on the basis of steric interactions and ring strain. The kinetics of the conversion of $[\text{Me}_2\text{Al}(\text{OPr}^n)]_3$ to $[\text{Me}_2\text{Al}(\text{OPr}^n)]_2$ have been investigated, $\Delta H^\ddagger$ and $\Delta S^\ddagger$ determined, and the identity of the reaction intermediates has been probed by NMR spectroscopy and mass spectrometry. <i>Ab initio</i> molecular orbital calculations have been carried out on the model compounds $[\text{H}_2\text{Al}(\mu\text{-OH})]_2$ 16 and $[\text{H}_2\text{Al}(\mu\text{-OH})]_3$ 17. The relative energies and calculated structures for 16 and 17 are considered in relation to experimental data.					
14. SUBJECT TERMS				15. NUMBER OF PAGES 9	
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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 5/18/93		3. REPORT TYPE AND DATES COVERED Technical Report	
4. TITLE AND SUBTITLE  The Preparation of $(Al_2O_3)_x(SiO_2)_y$ Thin Films Using $[Al(OSiEt_3)_3]_2$ as a Single Source Precursor				5. FUNDING NUMBERS  N00014-91-J-1934	
6. AUTHOR(S)  Christopher C. Landry, Linda K. Cheatham, Andrew N. MacInnes and Andrew R. Barron					
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)  Harvard University Department of Chemistry 12 Oxford Street Cambridge, MA 02138				8. PERFORMING ORGANIZATION REPORT NUMBER  3	
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11. SUPPLEMENTARY NOTES  Published in <u>Adv. Mater. Optics and Electronics</u> , 1992, <u>1</u> , 3					
12a. DISTRIBUTION / AVAILABILITY STATEMENT  Reproduction in whole or in part is permitted for any purpose of the United States government.. This document has been approved for public release and sale; its distribution is unlimited.				12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words)  Amorphous $(Al_2O_3)_x(SiO_2)_y$ thin films have been grown by atmospheric pressure metal-organic chemical vapor deposition using the single source precursor $[Al(OSiEt_3)_3]_2$ . Characterization by X-ray photoelectron spectroscopy indicated that the films consisted of a mixture of $Al_2O_3$ , $SiO_2$ and an aluminosilicate. The relative amount of each species was dependent on the deposition temperature and the carrier gas composition. Use of $NH_3$ as the carrier gas resulted in the increased volatility of the precursor by the <i>in situ</i> formation of the low melting Lewis acid-base adduct $Al(OSiEt_3)_3(NH_3)$ , however, no nitrogen incorporation was observed in these deposited films.					
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